I. BROMOSTILBENEDIOLS

II. STEREOCHEMISTRY OF THE MONOENOL, 1,2-DIMESITYL-1-PROPEN-1-OL

BY

RICHARD VERNON LINDSEY, JR.

A.B., Knox College, 1937

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE SCHOOL OF THE UNIVERSITY
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PART I

BROMOSTILBENEDIOLS

INTRODUCTION

When it was discovered that 1,2-dimesitylacetylene glycol was stable,[1,2] a program of exploratory research was instituted to discover the relation of the various structural features of the molecule to its remarkable behavior. One problem was to determine the effect of introducing substituents into the aromatic rings. This investigation deals with the incorporation of bromine atoms into various enediol molecules.

EXPERIMENTAL AND DISCUSSION OF RESULTS

3,3′-Dibromomesitil and 3,3′-dibromohexaethylbenzil were prepared by bromination of the corresponding hexaalkylbenzils. The structure of the former was proved by cleavage to 3-bromomesitoic acid with alkaline hydrogen peroxide.[3] The other benzil could not be cleaved.

By catalytic hydrogenation of 3,3′-dibromomesitil, either the *cis* or *trans* enediol could be obtained, depending on the duration of the reaction. In the ethyl series, the *trans* enediol was prepared by hydrogenation of the benzil but the *cis* isomer could not be obtained in this manner. It was prepared by reducing the benzil with the binary mixture, $Mg + MgI_2$. Results show that the introduction of the bromine atom into the meta position brought about no very great change in the behavior of the enediol.

cis-3,3′-Dibromohexamethylstilbenediol was caused to rearrange to 3,3′-dibromomesitoin which was oxidized to 3,3′-dibromomesitil. The ethyl analog could not be caused to rearrange.

Isomeric diacetates were prepared in each series. A dibenzoate of unknown configuration was prepared from dibromohexaethylstilbenediol. All diacetates were hydrolyzed with alkali.

The carbonate of *cis*-hexaethylstilbenediol was prepared by treating the iodomagnesium glycolate with oxalyl chloride. It is a new type of enediol derivative. No carbonate could be prepared from stilbenediol or hexamethylstilbenediol.

Unsuccessful attempts were made to prepare benzal and acetone derivatives, ethers, and phenylurethans of hexaethylstilbenediol.

Hexaethylbenzil has been cleaved to triethylbenzoic acid with hydrogen peroxide in glacial acetic acid solution.[4]

The possibility of measuring reduction potentials of enediol-diketone systems has been explored.

PART II

STEREOCHEMISTRY OF THE MONOENOL, 1,2-DIMESITYL-1-PROPEN-1-OL

INTRODUCTION

The observation that the stable vinyl alcohol,[5] 1,2-dimesityl-1-propen-1-ol, was structurally similar to the resolvable aryl olefins[6] suggested that a similar resolution might be effected in this case. An investigation was, therefore, initiated which had as its object the preparation and resolution of a suitable derivative of the monoenol.

EXPERIMENTAL AND DISCUSSION OF RESULTS

The methyl ether of 1-(3-carboxymesityl)-2-mesityl-1-propen-1-ol has been prepared by the following sequence of reactions: 3-bromomesitoyl chloride was alkylated by means of α^2-isoduryl-magnesium chloride to produce 3-bromodesoxymesitoin; condensation with paraformaldehyde followed by catalytic hydrogenation converted this ketone to the stable vinyl alcohol, 1-(3-bromomesityl)-2-mesityl-1-propen-1-ol, which was then methylated with dimethyl sulfate to produce the methyl ether of 1-(3-bromomesityl)-2-mesityl-1-propen-1-ol. Carbonation by the entrainment method of Grignard[7] replaced the nuclear bromine atom by a carboxyl group.

The acid was resolved through its quinine salt by fractional crystallization from acetone. The less soluble form of the salt had a specific rotation of —87.5° in ethanol at 27°. Decomposition of this salt by stirring repeatedly with dilute hydrochloric acid produced an acid having a specific rotation of +15° in ethanol at 27°. The acid underwent racemization in alcohol, loss of activity taking place in twenty-four hours at room temperature. It could not be recrystallized since racemization took place during this process.

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VITA

The author was born in Mt. Pulaski, Illinois, on April 20, 1916. He attended the public schools of Milford, Illinois, for one year, completed his elementary schooling at Pekin, Illinois, and was graduated from the Pekin Community High School in 1933. In the fall of 1933 he entered Knox College and received the degree of Bachelor of Arts in June, 1937. He enrolled in the University of Illinois in September of 1937, where he held a teaching assistantship from 1937 to 1939, a University Fellowship from 1939 to 1940, and the Abbott Laboratories Fellowship from 1940 to 1941.

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